

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 7/50, 7/26	A1	(11) International Publication Number: WO 95/07974 (43) International Publication Date: 23 March 1995 (23.03.95)
(21) International Application Number: PCT/US94/09954 (22) International Filing Date: 2 September 1994 (02.09.94) (30) Priority Data: 9319125.2 15 September 1993 (15.09.93) GB (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): KUEMIN, Marius, A., M. [CH/CH]; Sonnhaldenstrasse 23, CH-6331 Huenenberg (CH). SCHNEIDER, Michael [CH/CH]; Steinbruchstrasse 57, CH-8810 Horgen (CH). ALAM, Farooq [GB/CH]; Kirchstrasse 8, CH-8805 Richterswil (CH). CHARLES, Nelly, Rence [FR/FR]; 9, rue du Dauphiné, F-69330 Jonage (FR). (74) Agent: SHEPHERD, Philip, D.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, CA, CN, CZ, FI, HU, JP, KR, NO, PL, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CLEANING COMPOSITION (57) Abstract A cleaning composition comprises a (1) mono-, di- or tripropylene glycol n-butyl ether, (2) a solubilizer and (3) from 35 to 95 percent of water, based on the total weight of the cleaning composition. The solubilizer is a C ₁₋₃ -monoalkyl ether of mono-, di- or tripropylene glycol, a methyl ether acetate of mono-, di- or tripropylene glycol or a dimethyl ether of mono-, di- or tripropylene glycol. The cleaning composition is very useful for degreasing glass, metallic or polymeric articles.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

CLEANING COMPOSITION

The present invention relates to a cleaning composition and to the use of the cleaning composition for cleaning surfaces.

- 5 Cleaning compositions are widely used in the industry. Hard surfaces, such as glass, metallic or polymeric surfaces are often cleaned, either during finishing or prior to further processing, in order to remove traces of impurities like grease or salts. According to a frequent and simple cleaning method, the cleaning composition is applied on the surface to be cleaned and distributed with the aid of an absorbent object, such as a sponge, cloth or paper.
- 10 The cleaning composition should have a good wetting ability, a high cleaning efficiency and a fast and residue-free evaporation behavior. For example, it should not be necessary to rinse the surfaces with water or an organic solvent after cleaning.

WO 93/06204 discloses a cleaning composition which comprises (1) 30 to 70 volume percent of a glycol ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether or mixtures thereof, (2) 30 to 70 volume percent of one or more C₁₂₋₁₈ aliphatic hydrocarbons and (3) 0 to 10 volume percent of at least one surfactant. Metal parts are cleaned by subjecting the parts to a solvent wash with the described cleaning composition, blowing the washed parts with air, rinsing them with water and drying them.

The published German Offenlegungsschrift 37.17.600 relates to water-based hand cleansing compositions containing 4 to 20 weight percent of a water-soluble surfactant, 5 to 15 weight percent of a water-insoluble emulsifier, 10 to 20 weight percent of a hydrophilic organic solvent, 0 to 15 weight percent of a lipophilic oxygen-free organic solvent and 30 to 75 weight percent water. The hand cleansing compositions are said to be useful for removing paint, oil, grease, and tar from hands. Although these compositions may be useful for cleaning hands, they are less useful for cleaning glass, metallic or polymeric surfaces. Due to their high amount of high molecular emulsifiers and surfactants, such cleaning compositions leave an unacceptable level of residues upon drying or need a water rinse.

U.S. Patent 4,592,787 relates to a composition suitable for stripping cross-linked polymer which comprises

- 30 a) 40 to 75 weight percent of a lower alkyl monoether of a propylene glycol or a mixture of lower alkyl monoethers of propylene glycol;
- b) 10 to 30 weight percent of a C₂₋₆-alkanol;
- c) 4 to 28 weight percent of an alkanolamine and
- d) 1 to 14 weight percent of a base.
- 35 15 to 99 parts by weight of this composition may be diluted with 1 to 85 parts by weight of water. The function of the lower alkyl monoether of propylene glycol is to dissolve the adhesive and lift the photoresist polymer from the substrate. Many lower alkyl monoethers of

propylene glycol are listed, with propylene glycol isopropyl ether and propylene glycol methyl ether said to be preferred.

The published European patent application 0,407,952 relates to water-based compositions for stripping coatings and adhesives. They consist of from 40 to 80 weight percent of an aqueous surfactant solution containing one or more thickeners and 20 to 60 weight percent of a solvent mixture. The solvent mixture contains water-soluble and water-insoluble components. Exemplary of (partially) water-soluble components are ethylene carbonate, ethyl lactate, N-methyl-pyrrolidone or alkylene glycol alkyl ethers, such as mono- or dipropylene glycol monoalkyl ethers or diethylene glycol monoalkyl ethers. Exemplary of partially water-soluble or water-insoluble components are esters, ketones, terpenes, aromatic or aliphatic compounds, such as mono- or diacetates of ethylene glycol or propylene glycol. The viscosity of the stripping compositions is between 1000 and 4000 mPa·s. According to the examples these compositions contain a large number of various ingredients. However, the water-based compositions do not readily evaporate and have to be washed off after their use.

Many cleaning compositions have been suggested in the prior art which all require the presence of a non-volatile surfactant.

The published European Patent Application 0 066 342 discloses a general-purpose cleaning composition which is intended for use in cleaning hard surfaces, such as tiles, walls, floors, kitchen furniture, glass, and plastic-covered doors. The cleaning composition comprises 0.01 to 98 percent, most preferably 7 to 25 percent, by weight of a non-ionic surfactant, 0.005 to 20 percent, most preferably 0.5 to 10 percent, by weight of an at least partially esterified resin and 1 to 99.985 percent, most preferably 55-92.5, of a compatible liquid medium. The cleaning composition is said to have improved non-streak and cleaning properties. Preferred non-ionic surfactants consist of a hydrophobic moiety, such as a C₈-C₂₀ primary or secondary, branched- or straight-chain monoalcohol, a C₈-C₁₈ mono- or dialkylphenol, a C₈-C₂₀ fatty acid amide, and a hydrophilic moiety which consists of alkylene oxide units. The molecular weight of the esterified resin may vary from about a thousand to a few million. The compatible liquid medium may consist of water, or mixtures of water and one or more water-miscible organic solvents. Typical examples of such solvents are the lower aliphatic water-miscible alcohols, such as ethanol, propanol, isopropanol and butanol and glycols, such as ethylene- or propyleneglycol and glycolethers, such as the mono- and dimethyl-, -propyl-, -isopropyl-, -butyl-, isobutylethers of ethylene glycol, di- and triethylene glycol or analogous propylene glycol ethers.

GB-A-2,166,153 discloses a hard surface cleaning composition which essentially consists of 1 to 10 percent of a lower aliphatic monohydric alcohol having from 2 to 4 carbon atoms, 1 to 10 percent of propylene glycol monobutyl ether, 0.08 to 2.5 percent of a nonfluorinated anionic, non-ionic, amphoteric, ampholytic or zwitterionic surfactant, 0.003 to 2 percent of an anionic, non-ionic or cationic fluorinated hydrocarbon surfactant, 0.05 to 2

percent of a fungitive alkaline material, and the balance being water. All percentages are by weight.

U.S. Patent No. 5,108,660 discloses an aqueous hard surface detergent composition which comprises a hydrocarbyl-amidoalkylenesulfobetaine detergent surfactant, a cleaning solvent, a buffering system, water and optionally a nonaqueous polar solvent. Useful cleaning solvents are aromatic solvents, glycol ethers, such as mono- and dipropylene glycol monobutyl ether, monopropylene glycol monopropyl ether, mono- and diethylene glycol monohexyl ether and monoethylene glycol monobutyl ether and mixtures thereof. Particularly preferred cleaning solvents are diols having from 6 to 16 carbon atoms.

U.S. Patent No. 3,882,038 discloses a cleaner formulation which comprises 0.01 to 5 weight percent of a surfactant, 1 to 10 weight percent of at least one glycol ether solvent and 85 to 98.99 weight percent of water. The surfactant preferably is a polyethoxylated linear long chain alcohol surfactant.

U.S. patent No. 3,939,090 discloses an antifogging window cleaner which comprises 0.01 to 0.1 weight percent of a carboxyl-containing copolymer, up to 10 weight percent of at least one lower alkylene glycol alkyl monoether, such as ethylene glycol monobutyl or monomethyl ether, propylene glycol monomethyl or monobutyl ether, up to 25 weight percent of an aliphatic alcohol, 0.1 to 2 weight percent of an ethoxylated C₁₀₋₁₈ alkali metal sulfate and the balance water. The carboxyl-containing copolymer is a film former which hardens the window cleaner residue left on the glass at the time of application.

WO 91/15565 discloses an aqueous degreaser composition which comprises a sparingly soluble organic solvent, a solubilizing coupler and water. Preferred sparingly soluble organic solvents are 2-phenoxyethanol, 1-phenoxy-2-propanol, dipropylene glycol mono-butyl ether, n-butoxyethyl acetate and the dimethyl esters of mixed succinic, glutaric and adipic acids. Various sodium sulfonates, sulfates and phosphates are suggested as solubilizing couplers.

EP-A-0,347,110 discloses a concentrated liquid all purpose cleaning composition free of builder salts which comprises 16 to 30 weight percent of a water soluble detergent system, 5 to 15 weight percent of a water soluble organic solvent and 2 to 5.5 weight percent of a fragrance which has a pH of 6 to 7. The detergent system is a mixture of anionic and non-ionic surfactants. The anionic surfactant is a water-soluble salt, such as sodium paraffin sulfonate. The non-ionic surfactant is a condensation product of ethylene oxide and/or propylene oxide groups with an organic hydrophobic compound having terminal hydroxy groups. The organic solvent is a C₁₋₄-alkyl ether of ethylene or diethylene glycol or of mono-, di- or tripropylene glycol, such as dipropylene glycol n-butyl ether, diethylene glycol monobutyl ether or dipropylene glycol methyl ether.

U.S. Patent No. 4,863,629 discloses a cleaning composition which comprises from 1 to 20 weight percent of an anionic, non-ionic or amphoteric surfactant, 1 to 20 weight percent

of propylene glycol mono-tert-butyl ether, optionally mixed with a C₂₋₃ alcohol or a C₄₋₈ glycol ether, optional compounds like a solubilizer, a viscosity regulator, a complexing agent, further additives like perfume oils and water. Useful non-ionic surfactants are for example ethoxylated long-chain alcohols.

5 Unfortunately, all these above-described cleaning compositions comprise a substantial amount of surfactants or other non-volatile components which may leave an unacceptable level of residues upon drying.

Other skilled artisans have suggested volatile cleaning compositions which do not require the use of a non-volatile surfactant.

10 U.S. Patent No. 4,077,896 discloses a wax-stripping cleaning composition which contains 1 to 25 part by weight of a water-soluble monobutyl glycol ether, 2 to 20 parts by weight of a water-soluble primary amine and the remainder of 100 parts being water. The monobutyl glycol ether is preferably 2-butoxyethanol, diethylene glycol monobutyl ether or butoxyethoxy propanol. The U.S. 15 patent recommends the use of a surfactant, a thickening agent and a compatible water-soluble film-forming resin to inhibit the rapid evaporation of the water-soluble organic solvent and the primary amine. However, these recommended additives may leave unacceptable residues on the cleaned surface upon drying.

20 WO 93/25654, which has been published on December 23, 1993, discloses a homogeneous, aqueous cleaning composition which forms a solvent-water emulsion on evaporation of at least a portion of the solvent. The composition comprises a first solvent component in an amount that is present at a level above the miscibility limit of that component with water and a second solvent which is sufficiently volatile such that during use of the composition the second solvent component evaporates from the composition such that an 25 inhomogeneous mixture comprising the first solvent component and water is formed. The first solvent component preferably is mono- or dipropylene glycol n-butyl ether, mono- or dipropylene glycol mono-t-butyl ether, diethylene glycol hexyl ether, ethyl acetate or a mixture thereof. The second solvent component preferably is selected from volatile alcohols, water-miscible, volatile glycol ethers, aldehydes, ketones, dialkyl ethers or a mixture thereof. 30 More preferably, the second solvent component is methanol, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether and mixtures thereof.

FR-A-2,629,095 discloses a volatile aqueous cleaning composition for hard surfaces which does not comprise a surfactant. It comprises at least a volatile solvent and a volatile acid. Useful volatile solvents are C₁₋₄ alcohols, C₂₋₈ glycol ethers and mixtures thereof, 35 such as methanol, ethanol, isopropanol, butanol, ethylene glycol butyl ether, mono- and dipropylene glycol ethers and mixtures thereof. Useful volatile acids are mineralic acid, such as hydrochloric acid.

The published French Patent Application 2,571,279 relates to a cleaning agent for agricultural spraying apparatus, particularly to rinsing agents for spraying and atomizing assemblies. The cleaning agent comprises a propylene glycol ether or a mixture of such ethers. Disclosed examples are the methyl, ethyl, isopropyl, isobutyl and phenyl ether of propylene glycol, the methyl ether of di- and tripropylene glycol and propylene glycol methyl ether acetate. Thereof, the methyl ethers of propylene and dipropylene glycol and propylene glycol methyl ether acetate are said to be preferred. The ethers are preferably applied as 1 to 5 weight percent aqueous solutions.

Although these disclosed cleaning compositions are relatively efficient and do not require the use of a substantial amount of a non-volatile surfactant, it is desirable to provide a new highly efficient cleaning composition.

One aspect of the present invention is a cleaning composition which comprises (1) mono-, di- or tripropylene glycol n-butyl ether, (2) a solubilizer of C₁₋₃-monoalkyl ethers of mono-, di- and tripropylene glycol, methyl ether acetates of mono-, di- and tripropylene glycol or dimethyl ethers of mono-, di- and tripropylene glycol and (3) from 35 to 95 percent water, based on the weight of the cleaning composition. Preferably, the cleaning composition is essentially free of non-volatile additives.

Another aspect of the present invention is the use of the cleaning composition of the present invention for cleaning surfaces.

Yet another aspect of the present invention is a method of cleaning surfaces wherein an effective amount of the cleaning composition of the present invention is applied to the surface.

The cleaning composition of the present invention comprises mono-, di- or tripropylene glycol n-butyl ether. The term "glycol n-butyl ether" means the monoether. The monopropylene glycol n-butyl ether, simply called "propylene glycol n-butyl ether" is preferred. It has been found that at least the preferred embodiments of the cleaning composition of the present invention have a substantially better cleaning efficiency than corresponding cleaning compositions which contain another monoether of mono-, di- or tripropylene glycol instead of the n-butyl ether.

Furthermore, it has been found that the mono-, di- or tripropylene glycol n-butyl ether is substantially more effective for lowering the surface tension of water than most of the other propylene glycol monoethers. Lowering the surface tension of water is important for achieving good cleaning and evaporation results. When the surface tension of water is sufficiently lowered, a film is formed on the articles which quickly evaporates. When the surface tension of water is not lowered to a sufficient degree, droplets of water are formed which results in a slow evaporation. The cleaning composition preferably comprises from 1 to 40 percent, more preferably from 2 to 20 percent, most preferably from 2 to 8 percent of the mono-, di- or tripropylene glycol n-butyl ether, based on the total weight of the cleaning

composition. If the cleaning composition contains two or more of such n-butyl ethers, their total amount preferably is within the indicated ranges. The maximum amount of the n-butyl ether that is soluble in the cleaning composition depends on the amount of water and on the type and amount of the solubilizer. The amount of the n-butyl ether should generally be
5 chosen such that the cleaning formulation has a single phase. The maximum amount of the n-butyl ether that is soluble in the cleaning composition can be evaluated by series trials. For example, a cleaning composition comprising 60 percent water, propylene glycol n-butyl ether and, as a solubilizer, propylene glycol methyl ether forms a single phase when the amount of propylene glycol n-butyl ether is up to 18 percent and the amount of propylene glycol methyl
10 ether is at least 22 percent, based on the weight of the cleaning composition. When the cleaning composition contains 75 percent water, it forms a single phase when the amount of propylene glycol n-butyl ether is up to 7 percent and the amount of propylene glycol methyl ether is at least 16 percent, based on the weight of the cleaning composition. When the cleaning composition contains 90 percent water, it forms a single phase when the amount of
15 propylene glycol n-butyl ether is up to 5 percent and the amount of propylene glycol methyl ether is at least 5 percent, based on the weight of the cleaning composition.

The cleaning composition contains from 35 to 95 percent, preferably from 60 to 90 percent, more preferably from 70 to 80 percent of water, based on the total weight of the cleaning composition.

20 Further, the cleaning composition preferably contains from 4 to 60 percent, more preferably from 8 to 37 percent, most preferably from 12 to 28 percent of one or more solubilizers, based on the total weight of the cleaning composition. The solubilizer, sometimes called "coupler" by the skilled artisans, serves for increasing the solubility of the mono-, di- or tripropylene glycol n-butyl ether in water. The solubilizer selected for the present invention
25 also lowers the surface tension of water. It has been found that a useful solubilizer generally has a hydrophile/lipophile balance HLB of at least 7, preferably from 7.5 to 9.5. The solubilizer preferably forms an azeotrope with water and/or with the mono-, di- or tripropylene glycol n-butyl ether. By forming an azeotrope with water, the evaporation rate of water can be increased.

30 In the cleaning composition of the present invention, the solubilizer is C₁₋₃ monoalkyl ethers of mono-, di- and tripropylene glycol such as the methyl, ethyl, n-propyl and i-propyl ethers of mono-, di- and tripropylene glycol, the dimethyl ethers of mono-, di- and tripropylene glycol or the methyl ether acetates of mono-, di- and tripropylene glycol. The propylene glycol dimethyl ether is preferred over the dipropylene glycol dimethyl ether which
35 is preferred over the tripropylene glycol dimethyl ether. The most preferred acetate is propylene glycol methyl ether acetate.

The most preferred solubilizers are the methyl ethers of mono-, di- or tripropylene glycol, whereby the propylene glycol methyl ether is preferred over the

dipropylene glycol methyl ether which is preferred over the tripropylene glycol methyl ether. It has been found that these solubilizers increase the temperature stability of the cleaning composition of the present invention.

It has been found that other propylene glycol ethers would be less useful as solubilizers. For example, it has been found that mono-, di- and tripropylene glycol methyl n-butyl ethers are not useful because they are not sufficiently soluble in the cleaning composition of the present invention and their HLB is too low. The same applies, for example, to propylene glycol n-butyl ether acetate.

The cleaning composition of the present invention may additionally comprise a monofunctional alcohol as a solubilizer. Useful alcohols are mono- or multifunctional, saturated or unsaturated open-chain or cyclic alcohols, such as methanol, ethanol, the propanols, such as n-propanol or isopropanol, the butanols, such as n-butanol or isobutanol, allyl alcohol, furfuryl alcohol, crotyl alcohol or tetrahydrofurfuryl alcohol. The alcohol preferably has 1 to 8 carbon atoms. Isobutanol and the furfuryl alcohol are preferred.

The cleaning composition of the present invention may contain one or more types of solubilizers. Preferably, the total amount of solubilizers is within the above-mentioned ranges of from 4 to 60 percent, more preferably from 8 to 37 percent, most preferably from 12 to 28 percent, based on the total weight of the cleaning composition. Of this amount preferably from 0 to 10 percent, more preferably from 0 to 5 percent, most preferably from 0.5 to 3 percent of the cleaning composition is comprised of one of the above-mentioned monofunctional alcohols, most preferably isobutanol or furfuryl alcohol. The residual amount of solubilizers preferably consists of one or more glycol monoethers, most preferably of the methyl ethers of mono-, di- or tripropylene glycol.

The cleaning composition of the present invention optionally contains a corrosion inhibitor, preferably in an amount of from 10 to 500 ppm, preferably from 20 to 200 ppm, based on the total weight of the cleaning composition. Corrosion inhibitors for aqueous systems are well known in the art, for example nitrites, phosphates, borates, silicaborates or silicates. However, the cleaning composition of the present invention preferably comprises one or more organic basic buffers instead of a salt. Preferred organic basic buffers are amines, for example ammonia, ethylene diamine, hexamethylene tetraamine, benzotriazole, or mono-, di- or trialkanol amines, preferably mono- or triethanol amine or propanol amine. Monoethanol amine is the most preferred corrosion inhibitor.

The cleaning composition of the present invention may contain known optional additives, such as thickening agents, preservatives, bactericides, coloring agents, perfumes, surfactants or wetting agents, however, the cleaning composition of the present invention preferably is substantially free of non-volatile additives like high molecular additives or electrolytes. By "non-volatile additives" compounds are meant which do not evaporate to a noticeable degree at room temperature. By "substantially free" is meant that the amount of

non-volatile additives is preferably less than 80 ppm, more preferably less than 50 ppm, most preferably less than 30 ppm, based on the total weight of the cleaning composition.

Preferably, the mono-, di- or tripropylene glycol n-butyl ether, the solubilizer and water together amount to 90 percent or more, more preferably to 95 percent or more, most preferably to 99 percent or more, particularly to 99.5 percent or more of the total weight of the cleaning composition. Most preferably, the cleaning composition consists essentially of the mono-, di- or tripropylene glycol n-butyl ether, the solubilizer and water.

A preferred cleaning composition of the present invention comprises propylene glycol n-butyl ether, propylene glycol methyl ether, isobutanol, water and a corrosion inhibitor, preferably ethanol amine. The most preferred cleaning composition comprises from 5 to 8 percent of propylene glycol n-butyl ether, from 15 to 20 percent of propylene glycol methyl ether, from 0.5 to 2 percent of isobutanol, from 70 to 80 percent of water and from 50 to 150 ppm of a corrosion inhibitor, based on the total weight of the cleaning agent.

The cleaning composition of the present invention is usually prepared by mixing the various ingredients. Typically the ingredients are mixed at room temperature. The cleaning composition of the present invention is very useful for removing polar and non-polar impurities, such as grease, oils or salts from hard surfaces of articles, such as glass, metallic or polymeric surfaces. The cleaning composition is particularly useful for removing impurities from metallic surfaces prior to processes which require clean and dry surfaces, such as gluing or painting. The cleaning composition can be applied to the surface to be cleaned in any known manner. For example, the cleaning composition may be applied to and/or distributed on the surface to be cleaned with a spraying device or an absorbent object, such as a sponge, cloth, paper, or piece of leather. Although the cleaning composition may be used at decreased or slightly elevated temperatures, it is preferably used at room temperature for cleaning purposes. The cleaning composition is preferably distributed on and/or at least partially removed from the surface by wiping with an absorbent object. The cleaning composition of the present invention has a very good cleaning capability and quickly evaporates after cleaning. Due to its fast drying behavior, the cleaning composition is very useful for cleaning articles which will be further processed, for example in a gluing or painting process. At least the preferred embodiments of the cleaning composition which are essentially free of high molecular additives and/or electrolytes do not leave residues on the surfaces of the cleaned articles. Furthermore, most of the cleaning compositions of the present invention have a sufficiently high flash point in order not to be a very high fire hazard. The cleaning compositions of the present invention generally have a flash point of more than 40°C, typically of more than 50°C at atmospheric pressure. Cleaning compositions which have a flash point of at least 55°C are preferred.

The present invention is further illustrated by the following examples which should not be construed to limit the scope of the present invention. Unless otherwise mentioned, all parts and percentages are by weight.

5 The cleaning efficiency according to the IPP test, the surface tension and the evaporation rate of the various cleaning compositions are measured as follows.

The IPP test is published in "Seifen, Oele, Fette, Wachse, Heft 10/1986, pages 371-372, Qualitätsnormen für Fussbodenpflege- und Reinigungsmittel". A white carrier is treated with defined impurities. The contaminated carrier is wiped with a sponge which has been soaked with the cleaning composition under well defined conditions. The cleaning effect
10 is measured photoelectrically in comparison with a white carrier which has not been treated with impurities (= 100 percent). The higher the number is that is achieved by a specific cleaning composition in the IPP test, the better is its cleaning efficiency.

The surface tension of the cleaning compositions is measured at 20°C according to DIN 53 914. Low surface tensions are preferred.

15 To measure the evaporation rate in minutes as listed in Tables 1 and 3, a cold rolled steel plate of the size of 12 x 20 cm is marked with a gradation line. A solvent composition is poured on the plate in a horizontal position. The plate is then suspended from a corner and the solvent is allowed to clear from the plate by dual action of drying and solvent draining.

20 Examples 1 to 3 and Comparative Examples A to Q

In a Series I various cleaning compositions are prepared consisting of 5 percent of a glycol ether listed in Table I below, 20 percent of propylene glycol methyl ether and 75 percent of water. The cleaning efficiency according to the IPP test and the surface tension of the cleaning compositions of Series A is listed in Table I below.

25 In a Series II various mixtures are prepared consisting of 5 percent of a glycol ether listed in Table 1 below and 95 percent water. The mixtures of Series II are prepared for further evaluating the cleaning efficiency of various glycol ethers and their capability of lowering the surface tension of water. The cleaning efficiency of the mixtures of Series II according to the IPP test and their surface tension is also listed in Table I below.

30 For information purposes the surface tension of various undiluted glycol ethers, their HLB and their ability to form an azeotrope with water are listed in Table I as well.

TABLE I

Example	Glycol ether	Series I IPP test	Series I Surface tension (mN/m)	Series II IPP test	Series II Surface tension (mN/m)
1	propylene glycol n-butyl ether	63	28.6	64	28.8
2	dipropylene glycol n-butyl ether	66	28.7	60 ¹⁾	29.8
3	tripropylene glycol n-butyl ether	67	28.7	*)	*)
A	propylene glycol methyl ether	33	41	29	50
B	propylene glycol tert. butyl ether	56	31.8	27	36.6
C	propylene glycol isobutyl ether	53	27.8	*)	*)
D	propylene glycol ethyl ether	51	36.1	27	50.4
E	propylene glycol n-propyl ether	57	33	42	36.2
F	propylene glycol isopropyl ether	51	33.9	17	41.1

*) two phase system

-) not measured

¹⁾ 4.6% dipropylene glycol n-butyl ether dissolved

TABLE I - Continued (I)

Example	Glycol ether	Surface tension of glycol ether 100% (mN/m)	HLB of glycol ether	Azeotrope with H ₂ O
1	propylene glycol n-butyl ether	27.6	6.9	yes
2	dipropylene glycol n-butyl ether	29.2	6.8	-
3	tripropylene glycol n-butyl ether	29.9	6.6	-
A	propylene glycol methyl ether	28.3	8.3	yes
B	propylene glycol tert-butyl ether	24.2		yes
C	propylene glycol isobutyl ether	23.7		-
D	propylene glycol ethyl ether	24.6		-
E	propylene glycol n-propyl ether	24.3		-
F	propylene glycol isopropyl ether	21.9		-

*) two phase system

-) not measured

1) 4.6% dipropylene glycol n-butyl ether dissolved

TABLE I - Continued (II)

Example	Glycol ether	Series I IPP test	Series I Surface tension (mN/m)	Series II IPP test	Series II Surface tension (mN/m)
G	ethylene glycol n-butyl ether	51	-	53	33.2
H	diethylene glycol n- butyl ether	56	-	48	35.7
I	propylene glycol dimethyl ether	-	-	29	33.2
J	propylene glycol methyl n-butyl ether	*)	*)	*)	*)
K	propylene glycol methyl ether acetate	-	-	39	42
L	propylene glycol n- butyl ether acetate	-	-	*)	*)
M	dipropylene glycol methyl ether	-	-	29	45.4
N	dipropylene glycol dimethyl ether	- -		30	46.2
O	dipropylene glycol methyl n-butyl ether	*)	*)	*)	*)
P	tripropylene glycol methyl ether	-	-	33	-
Q	tripropylene glycol methyl n-butyl ether	-	-	*)	*)

*) two phase system

-) not measured

1) 4.6% dipropylene glycol n-butyl ether dissolved

TABLE I - Continued (III)

Example	Glycol ether	Surface tension of glycol ether 100% (mN/m)	HLB of glycol ether	Azeotrope with H ₂ O
G	ethylene glycol n-butyl ether	27.4	7.4	yes
H	diethylene glycol n-butyl ether	30	7.7	-
I	propylene glycol dimethyl ether	-	7.2	-
J	propylene glycol methyl n-butyl ether	20.6	5.8	-
K	propylene glycol methyl ether acetate	29.4	8.3	-
L	propylene glycol n-butyl ether acetate	24.7	6.9	yes
M	dipropylene glycol methyl ether	22.1	8.2	yes
N	dipropylene glycol dimethyl ether	26.8	7.1	yes
O	dipropylene glycol methyl n-butyl ether	22.1	5.7	-
P	tripropylene glycol methyl ether	30.9	8.2	-
Q	tripropylene glycol methyl n-butyl ether	23.4	5.5	-

*) two phase system

-) not measured

1) 4.6% dipropylene glycol n-butyl ether dissolved

The results of Series I illustrate that the cleaning compositions of the present invention comprising mono-, di- or tripropylene glycol n-butyl ether have a considerably better cleaning efficiency than comparable compositions which contain another glycol ether.

Examples 1-3 show a substantially better result in the IPP test than Comparative Examples A-H.

- 5 Furthermore, the cleaning composition of the present invention generally have a lower surface tension than comparable compositions which contain another glycol ether. The surface tension of Comparative Example C is equally low, however, its cleaning efficiency in the IPP test is not satisfactory.

- 10 The results of Series II illustrate that the cleaning efficiency of an aqueous solution of mono- or di-propylene glycol n-butyl ether is considerably better than the cleaning efficiency of comparable aqueous solutions containing other glycol ethers. Furthermore, aqueous solutions of mono- or dipropylene glycol n-butyl ether have a considerably lower surface tension than comparable aqueous solutions containing other glycol ethers.

Examples 4 to 8

- 15 The cleaning efficiency of various cleaning compositions of the present invention are listed in Table 2 below.

TABLE II

Example	Glycol ether x	IPP test 90% water, 5% propylene glycol n-butyl ether, 5% glycol ether x	IPP test 75% water, 5% propylene glycol n-butyl ether, 20% glycol ether x
4	propylene glycol methyl ether	69	63
5	propylene glycol dimethyl ether	69	-
6	propylene glycol methyl ether acetate	71	-
7	dipropylene glycol methyl ether	67	53
8	dipropylene glycol dimethyl ether	68	-

-) not measured

Table II illustrates that not only good results are achieved in the IPP test when the cleaning composition contains propylene glycol methyl ether as a solubilizer but also when it contains other solubilizers within the scope of the present invention.

Examples 9 to 41 and Comparative Example R

5 Table III below lists the compositions of various cleaning compositions of the present invention, their cleaning efficiency in the IPP test, their flash points, evaporation in minutes and their surface tension. The flash points are measured on a Pensky-Martens closed-cup PMCC apparatus according to DIN 51758.

TABLE III

Example	% Water	% DMM 1)	% DPM 2)	% PM 3)	% PnB 4)	% isobutanol
R	80	20				
9	65	16	11		8	
10	80		10		10	
11	10			45	45	
12	10		45		45	
13	50			25	25	
14	50		25		25	
15	80			15	5	
16	80		15		5	
17	84	4	4		4	4
18	80	4		10	6	
19	80	4	10		6	
20	27	20		40	10	3
21	60	5		25	8	2
22	69.5	5		18	7	0.5
23	80	3.3		11.8	4.6	0.3

1) DMM: dipropylene glycol dimethyl ether

2) DPM: dipropylene glycol methyl ether

3) PM: propylene glycol methyl ether

4) PnB: propylene glycol n-butyl ether

5) n-butyl acetate instead of isobutanol

TABLE III - Continued (I)

Example	IPP test	Flash point (°C)	evaporation (Min)	Surface tension mN/n
R	44		8	
9	76	79	32	
10	77		17	
11	82	52	11	
12	79			
13	75	62	13	27.1
14	78			
15	68	65	7	
16	60		19	
17	74	41		
18	71	66		
19	73			
20	79	53	4.5	
21	76	53	6.5	
22	88	59	12	
23	74	61	8.3	

1) DMM: dipropylene glycol dimethyl ether

2) DPM: dipropylene glycol methyl ether

3) PM: propylene glycol methyl ether

4) PnB: propylene glycol n-butyl ether

5) n-butyl acetate instead of isobutanol

TABLE III - Continued (II)

Example	% Water	% DMM 1)	% DPM 2)	% PM 3)	% PnB 4)	% isobutanol
24	70			21.2	8.2	0.6
25	69.5	5	18		7	0.5
26	70	5		18	7	
27	70.5	4		18	7	1.5
28	70			20	8	2
29	70.5			20	8	1.5
30	75			16.7	6.7	1.6
31	79.7			13.3	5.3	1.66
32	70.5		15	5	8	1.5
33	71.5			20	8	0.5 5)
34	80		10.5	3.5	6	
35	80	3		12	5	
36	75			17.5	6.5	1.0
37	80			14	5.2	0.8
38	80		13.5		6.5	
39	75		20		5	
40	72		20		8	
41	75		10	10	5	

1) DMM: dipropylene glycol dimethyl ether

2) DPM: dipropylene glycol methyl ether

3) PM: propylene glycol methyl ether

4) PnB: propylene glycol n-butyl ether

5) n -butyl acetate instead of isobutanol

TABLE III - Continued (III)

Example	IPP test	Flash point (°C)	evaporation (Min)	Surface tension mN/n
24	88	58	12	
25	75	97	>30	
26	80	62	10	
27	93	57	9	
28	86	55	9.5	26.8
29	74	56	9.5	
30	73	55	7	
91	72	56	7	
32	80	61		
33	69	51		
34	70	99		27.9
35	61	63		
36	71	59	7	26.7
37	58	60		
38	70	99		
39				29.0
40				27.3
41				28.9

1) DMM: dipropylene glycol dimethyl ether

2) DPM: dipropylene glycol methyl ether

3) PM: propylene glycol methyl ether

4) PnB: propylene glycol n-butyl ether

5) n-butyl acetate instead of isobutanol

30

Table III illustrates the good results of the compositions of the present invention in the IPP test (in the range of 58 and 93) whereas the composition of Comparative Example R only reaches 44 in the IPP test. Further, Table III illustrates that most of the cleaning compositions of the present invention have a relatively high flash point (55°C or more) and, accordingly, are not a high fire hazard.

Table IV illustrates the evaporation rates of

- undiluted water,
- the cleaning composition of Example 36 (75 percent water, 17.5 percent propylene glycol methyl ether, 6.5 percent propylene glycol n-butyl ether and 1 percent isobutanol),
- undiluted propylene glycol n-butyl ether,
- a mixture of 5 percent propylene glycol n-butyl ether and 95 percent water,
- a mixture of 25 percent propylene glycol n-butyl ether and 75 percent water,
- undiluted propylene glycol methyl ether,
- a mixture of 5 percent propylene glycol n-butyl ether and 95 percent water and
- a mixture of 25 percent propylene glycol n-butyl ether and 75 percent water.

The evaporation rates listed in Table IV are measured by a method similar to ASTM 3539. Table IV lists the amount of liquid that is left (that is, that has not evaporated) versus the time period during which the liquid is allowed to stand at 25°C.

TABLE IV

time min	water	Ex 36 1)	100% PnB 2)	5% Pnb in water
0	100	100	100	100
5	85.6	81.1		83.1
10	71.7	62.1	89.8	66.4
15	57.3	44.4		51.1
20	43.3	28.1	80.7	36.4
25	30.7	15.5		24.1
30	19.7	6.5	72	13.8
35	10.5			6.7
40	3.8		63.9	
45				
50			55.8	
55				
60			47.9	
65				
70			40.5	
75				
80			33.2	
85				

1) 75% water, 17.5% PM, 6.5% PnB and 1.0% isobutanol

2) PnB: propylene glycol n-butyl ether

3) PM: propylene glycol methyl ether

TABLE IV - Continued

	time min	25% PnB in water	100% PM ³⁾	5% PM in water	25% PM in water
5	0	100	100	100	100
	5	83	70.7	87.8	85.9
	10	65	42.2	75.4	72.2
	15	48	19.8	62.9	58.1
	20	33.1	4	51.1	45.4
10	25	20.4		39.5	33.4
	30	11		28.8	22.9
	35			19.8	7.3
	40			11.7	
	45			5.1	
15	50				
	55				
	60				
	65				
20	70				
	75				
	80				
	85				

1) 75% water, 17.5% PM, 6.5% PnB and 1.0% isobutanol

2) PnB: propylene glycol n-butyl ether

3) PM: propylene glycol methyl ether

As illustrated by Table IV, after 30 minutes 93.5 percent of the cleaning composition of Example 36 have evaporated (that is, 6.5 percent are left). The cleaning composition of Example 36 contains 17.5 percent of propylene glycol methyl ether and 6.5 percent of propylene glycol n-butyl ether, i.e. totally about 25 percent glycol monoether.

When the composition contains 25 percent of propylene glycol n-butyl ether, after 30 minutes only 89 percent of the composition have evaporated. When the composition contains 25 percent of propylene glycol methyl ether, after 30 minutes only 77.1 percent of the composition have evaporated. The increased evaporation rate of the cleaning composition of Example 36 can also be observed after 5, 10, 15, 20 and 25 minutes. Apparently, propylene glycol methyl ether and propylene glycol n-butyl ether have a synergistic effect on the evaporation rate of aqueous compositions containing such propylene glycol monoethers.

Claims:

1. A cleaning composition comprising
(1) mono-, di- or tripropylene glycol n-butyl ether,
(2) a solubilizer selected from the group consisting of a C₁₋₃-monoalkyl ether of
mono-, di- and tripropylene glycol, a methyl ether acetate of mono-, di- and a
5 tripropylene glycol or dimethyl ether of mono-, di- and tripropylene glycol and
(3) from 35 to 95 percent of water, based on the total weight of the cleaning
composition.
2. The cleaning composition of Claim 1 being essentially free of non-volatile
additives.
- 10 3. The cleaning composition of Claim 1 or Claim 2 comprising from 1 to 40
percent of the mono-, di- or tripropylene glycol n-butyl ether, based on the total weight of the
cleaning composition.
4. The cleaning composition of any one of Claims 1 to 3 comprising from 4 to
60 percent of the solubilizer, based on the total weight of the cleaning composition.
- 15 5. The cleaning composition of any one of Claims 1 to 4 wherein the
solubilizer is the methyl, ethyl, n-propyl and i-propyl ether of monopropylene glycol,
dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, monopropylene
glycol methyl ether acetate, monopropylene glycol dimethyl ether or dipropylene glycol
dimethyl ether.
- 20 6. The cleaning composition of Claim 5 wherein the solubilizer is mono-, di- or
tripropylene glycol monomethyl ether.
7. The cleaning composition of Claim 6 wherein the solubilizer is
monopropylene glycol monomethyl ether.
8. The cleaning composition of any one of Claims 1 to 4 comprising
25 monopropylene glycol
mono-n-butyl ether, monopropylene glycol monomethyl ether, isobutyl alcohol, a corrosion
inhibitor and water.
9. Use of the cleaning composition of any one of Claims 1 to 8 for cleaning a
surface.
- 30 10. The use of Claim 9 wherein the cleaning composition is distributed on
and/or at least partially removed from the surface by wiping with an absorbent object.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/09954

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C11D7/50 C11D7/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 882 038 (E.T. CLAYTON ET AL.) 6 May 1975 cited in the application see column 6, line 42 - line 54 see column 7, line 35 - line 45 ---	1-3,9,10
A	WO,A,91 15565 (BUCKEYE INTERNATIONAL) 17 October 1991 cited in the application see page 6, line 1 - page 7, line 8; claims 1,6-8,11,22 ---	1-3,9,10
A	US,A,4 077 896 (F.J. BUNEGAR ET AL.) 7 March 1978 cited in the application see claims 1,2 --- -/--	1-3,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

11 January 1995

Date of mailing of the international search report

24.01.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/09954

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO,A,93 25654 (UNILEVER) 23 December 1993 cited in the application see claims 1-6,13,15; examples -----	1-3,9,10
A	FR,A,2 629 095 (RECKITT & COLMAN) 29 September 1989 cited in the application see claims ---	1-3
A	EP,A,0 347 110 (COLGATE-PALMOLIVE) 20 December 1989 see examples 1,23 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/09954

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3882038	06-05-75	NONE	
WO-A-9115565	17-10-91	US-A- 5080822 AU-A- 7694991 EP-A- 0525032	14-01-92 30-10-91 03-02-93
US-A-4077896	07-03-78	AU-B- 504065 AU-A- 1028076 GB-A- 1535274 JP-A- 51096807 JP-B- 58042239	04-10-79 21-07-77 13-12-78 25-08-76 17-09-83
WO-A-9325654	23-12-93	AU-B- 4318493 AU-B- 4708593 WO-A- 9404644	04-01-94 15-03-94 03-03-94
FR-A-2629095	29-09-89	NONE	
EP-A-0347110	20-12-89	AU-B- 627734 AU-A- 3599189	03-09-92 14-12-89